

DATE:

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TO:

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FROM:

Ex. 4 - CBI

THOUGH:

SUBJECT:

Ex. 6 - Personal Privacy RESIDENCES WELL WATER TREATMENT SYSTEM

EVALUATIONS - TRIP REPORT

DIMOCK RESIDENTIAL GROUNDWATER SITE, DIMOCK, PA

Work Assignment No.: SERAS-172

PURPOSE

Lockheed Martin's Scientific, Engineering, Response and Analytical Services (SERAS) contract personnel were tasked by the Environmental Protection Agency/Environmental Response Team (EPA/ERT) and EPA Region 3 to assist with the evaluation of the point-of-entry (POE) water treatment systems at two [Ex. 6 · Personal Privacy] residences in Dimock, Pennsylvania (PA) that have relied upon and drawn drinking/potable water from a single private well HW08. In recent years however, the water in HW08 has been found to be impacted with elevated levels of manganese (Mn). HW08 has also exhibited offgassing/presence of methane (CH₄), a constituent of natural gas. The purpose of this Trip Report is to detail the observations made by SERAS personnel at the [Ex. 6 · Personal Privacy] residences in early July 2012 during the period when the existing POE systems were scheduled for maintenance and testing upon reconnection to well water supply.

BACKGROUND

The Dimock Residential Groundwater site is located in a rural/residential area of Dimock, PA, Susquehanna County, off of PA-29. Residents within a 9 square mile area have been experiencing increased methane gas in their private drinking water supply wells. Consequently, a moratorium has been placed in this area on natural gas drilling operations. Concerns have risen about other contaminants in drinking water samples collected by Cabot Oil and Gas and the Pennsylvania Department of Environmental Protection (PADEP). The USEPA Region 3 has initiated further investigations into the residential drinking water issue.

SITE ACTIVITIES AND OBSERVATIONS

On Monday, July 2, 2012, **Ex. 4-CBI** a SERAS Project Engineer, traveled to the site. He met with Mr. Richard Rupert, Mr. Richard Fetzer and Ms. Kelly Chase of EPA Region 3 and Dave Bofinger of Kemron Environmental Services, Inc. at the command post in South Montrose, PA. Early that afternoon, Mr. [Ex. 4-CBI] Mr. Rupert, Mr. Fetzer and Mr. Bofinger travelled to two **Ex. 4-CBI** residences in Dimock, PA. The following residences were visited:

| CR644 - | Ex. 6 - Personal Privacy | | | | |
|-------------|--------------------------|--------------------------|--|--|--|
| CR652 - | A trailer home at | Ex. 6 - Personal Privacy | | | |
| System Main | tenance (July 2, 2012). | | | | |

- Ex. 4 CBI and his assistant, personnel from Ex. 4 CBI, were at the homes to service the POE systems. The Ex. 4 CBI team was observed to perform the following maintenance work on each system, first at CR644 and then at CR652:
 - The liquid-phase granular activated carbon (LGAC) canister was replaced with a fresh LGAC canister containing approximately 40 lbs of GAC.
 - The 35-gallon chlorine feed tank (CFT) was temporarily taken off-line, cleaned out, put back online and filled with approximately 35 gallons (gal) of chlorine solution (CS). The CS was made up of 7.1 gal of Clorox (High Efficiency Bleach) (5 x 1.42 gal each jug) and 28 gal of potable water from the potable water tank (PWT). The resulting composition of the CS was (1:4) or 1 part Clorox to 4 parts water.
 - The plumbing for each system was checked and adjusted/repaired as needed.
 - Both systems were turned on. At this point, water from the PWT (EPA supplied potable water) was allowed to run through the system to ensure all the plumbing and the system components including the chlorine feed pump (CFP) were working. This concluded the system maintenance work.

As per the [Ex.4-CBI] technician, the system operation involves:

- The controller on top of the LGAC tank is programmed to automatically back-flush the LGAC unit once a week.
- The two 40-gal chlorine contact tanks (CCT) (installed in parallel) require manual back-flushing once-a-day by the home owner.
- The back-flushing of the LGAC canister and the CCTs is required to remove any sediment (precipitated material such as oxides of Mn and iron (Fe), for example) that built up in the system. The back-flushed sediments are released to the ground immediately underneath the respective trailers.
- When the level in the 35-gal CFT is down to 20 percent (%) or one fifth, the home owner is required to add 4 x 1.42-gal Clorox jugs to the CFT and top it off with water to bring it to the 35-gal mark. Alternatively, if the level in the CFT is at 40%, the home owner would add 3 x 1.42-gal Clorox jugs to the CFT and top it off with water.
- The operation of the CFP is triggered by a flow-sensor switch installed on the incoming water supply line. Typically, the entire system is under pressure which ensures that water is always available on-demand at any faucet or tap in the home. Therefore, whenever a tap or faucet is opened, makeup water is drawn in through the POE system. When this happens, the flow-sensor, upon sensing the flow, turns ON the CFP, thereby injecting fresh chlorine solution into the incoming untreated water stream just before it enters the CCTs.

- Presence of chlorine in the water facilitates the oxidation of dissolved metals such as Mn and Fe resulting in formation and subsequent precipitation of their respective insoluble oxides. Typically, the bulk of the sediments settle out at the bottom of the CCTs, and thus the need for their daily back-flushing. The carry-over sediments from the CCTs are filtered out at the bottom of the LGAC unit, and thus the need for its weekly back-flushing.
- Unreacted or excess chlorine in the water leaving the CCTs is removed by the LGAC unit. Over time, the GAC's chlorine absorption capacity is exhausted and it needs to be replaced with fresh GAC.

System Startup and Water Flowrate Check. On the morning of Tuesday, July 3, 2012, Mr. [Ex.4-CB] Mr. Rupert and Mr. Bofinger arrived at the [Ex.5-Parasoul Privacy] residences.

At 0845, Mr. Bofinger shut off the water supply from the PWT to CR644, and instead connected the line from well HW08 to CR644. At CR644, the kitchen sink faucet was turned ON, and remained ON until the end of the testing period. The water flowrate was measured at 1.43 gal per minute (gpm) [1 gal in 42 seconds]. At this flowrate, the residence time (RT) for the chlorinated water before it enters the LGAC is approximately 56 minutes [80 gal / 1.43 gpm]. [NOTE: Both CR644 and CR652 water treatment systems have two (2) 40-gal chlorine contact tanks in parallel, providing a combined contact tank capacity of 80 gal.].

At 0905, Mr. Bofinger shut off the water supply from the PWT to CR652, and instead connected the line from well HW08 to CR652. At CR652, the bathtub faucet was turned ON, and remained ON until the end of the testing period. The initial flowrate was measured at about 3.96 gpm. The flow rate was turned down and set to 2 gpm [2 gal in 61 seconds]. At this flowrate, the residence time (RT) for the chlorinated water before it enters the LGAC is approximately 40 minutes [80 gal / 2 gpm].

Several hours later, at the conclusion of the POE system testing and water sample collection (see discussion under Water Sampling by TechLaw), the water flow rates at the CR644 kitchen sink and the CR652 bathtub faucets were rechecked. At both locations, the flow rates were practically unchanged, 1.43 gpm at the CR644 kitchen sink faucet and 2 gpm at the CR652 bathtub faucet.

Following the completion of the water sampling, water flows at the CR644 kitchen sink and the CR652 bathtub faucets were turned OFF. Mr. Bofinger disconnected the well water supply connection to both homes, and instead reconnected them to the PWT. Once again, the CR644 kitchen sink and the CR652 bathtub faucets were turned ON, and left running for several hours, to purge both POE systems completely of the well water, before the homeowners were allowed to use the water in their respective homes. This was done as a precaution to prevent inadvertent exposure of the residents to the known contaminants in HW08, at least until the test results were received, reviewed and the performance of the POE systems were evaluated.

Well Water Temperature Checks.

At 0930, water temperature at HW08 well head was 52 degrees Fahrenheit (°F). At 0935, water temperature at the PWT outlet was 69.5°F.

Methane (CH₄) Monitoring with TVA-1000b and GEM-2000.

A toxic vapor analyzer TVA-1000b from Thermo Scientific, which uses a flame ionization detector (FID), was used primarily to screen for the presence of methane (CH₄) gas off-gassing from the water from well HW08, and as it travels through the POE system. Typically, the TVA-1000b measures the sum total concentration of all hydrocarbons to which the FID responds to. However, for this project, the TVA was fitted with a GAC (charcoal) filter tip allowing it to see only methane (and/or ethane if present) while

filtering out other hydrocarbons. The TVA-1000b is designed to detect CH₄ from 0.5 to 50,000 ppm_v [or 5 percent (%)]. The TVA-1000b fitted with a charcoal filter tip was calibrated using a 500 parts per million by volume (ppm_v) CH₄ standard at the SERAS Air Toxic Laboratory, in Edison, New Jersey, just prior to deployment to the field.

A landfill gas monitor GEM-2000 from CES-Landtec, which uses an Infrared Gas Analyzer (IGA), was also used to screen a limited number of vapor samples. Unlike the TVA-1000b, the GEM-2000 is specifically designed to detect CH₄, carbon dioxide (CO₂) and oxygen (O₂). It will detect CH₄ from 0 to 100 %, with a resolution of 0.1% or 1,000 ppm_y.

Typically, the TVA-1000b measures the sum total concentration of all hydrocarbons to which the FID responds to. However, for this project, the TVA was fitted with a GAC (charcoal) filter tip allowing it to see only methane (and/or ethane if present) while filtering out other hydrocarbons. At the Ex.6-Personal Privacy residences, CH₄ was the primary suspected gas of concern, and thus, concentration of gas measured using the TVA-1000b was assumed to be that of CH₄.

Instrument Readouts

The TVA-1000b provides CH_4 readings in either ppm_v or %. If the vapor phase concentration is less than 1%, the reading is displayed on the TVA-1000b screen as ppm_v . The GEM-2000 on the other hand, provides CH_4 readings only as %, with a resolution of 0.1%. In the field, the readings were logged in the original display units. However, for the purpose of uniformity, CH_4 readings reported in tables below have been presented as ppm_v . [Note: Vapor phase concentration of $1\% = 10,000 \ ppm_v$]. Also, during each CH_4 screening, once the probe tip of the analyzer (TVA-1000b or GEM-2000 as the case may be) was inserted into the head space of the sample bottle, the CH_4 readings on the display screen were closely observed. When CH_4 was present, the instrument readout showed a quick rise in the concentration up to a peak value before it drops off. The vapor phase CH_4 readings logged were the peak values.

Methane in Background Air

At 1000, background CH₄ level in the air around CR644 and CR652 was between 2 and 3 ppm_v, and ambient temperature was approximately 82°F.

At HW08 Well Head

At 1010, water from well HW08 was allowed to run through the attached garden hose for a couple of minutes to thoroughly purge the hose and for the hose discharge water temperature to equilibrate with the well head temperature.

At 1015, a 1-gal narrow-mouth plastic jug was filled with the HW08 well water. Temperature of the water was measured. Then, one half of the jug was emptied and a cap was immediately placed on the jug. Through a small hole (approximately 0.25 inch diameter) in the cap, the TVA 1000b probe was inserted into the head space of the jug to check for the CH₄ level (unshaken results). Soon after, the contents of the jug were vigorously shaken, and the head space of the jug was screened for the CH₄ level (shaken results). Readings are as follows:

| Time | Temp | TVA-1000b | GEM-2000 | Comments | |
|------|------|--|--|----------|--|
| | (°F) | CH ₄ (peak ppm _v) | CH ₄ (peak ppm _v) | | |
| 1015 | 50 | 40,000 | ~ | Unshaken | |
| 1018 | 51 | 15,000 | ~ | Shaken | |
| | | | | | |
| 1137 | 51 | 1,400 | 1,000 | Unshaken | |
| 1138 | 51 | 88,000 | 49,000 | Shaken | |

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At CR644, By-Pass/Pre-LGAC Sample Tap (i.e., down-stream of chlorine contact tank and upstream of the LGAC/de-chlorination vessel.

| Time | Temp | TVA-1000b | GEM-2000 | Comments | |
|------|------|--|--|-------------------------------------|--|
| | (°F) | CH ₄ (peak ppm _v) | CH ₄ (peak ppm _v) | | |
| 1016 | 56 | 400 | ~ | Shaken | |
| 1023 | 56 | 1,300 | ? | Unshaken | |
| 1024 | 56 | 13,000 | ~ | Shaken | |
| | | | | | |
| | | | | 15 minutes after water was shut off | |
| | | | | at the CR644 Kitchen Sink Faucet. | |
| 1307 | 57 | 764 | 1,000 | Unshaken | |
| 1308 | 57 | 21,000 | 31,000 | Shaken | |

At CR644, Kitchen Sink Faucet.

| Time | Temp | TVA-1000b | GEM-2000 | Comments | |
|------|------|--|--|-------------------------|--|
| | (°F) | CH ₄ (peak ppm _v) | CH ₄ (peak ppm _v) | | |
| 1021 | 58 | 31 | ? | Unshaken | |
| 1022 | 58 | 1,800 | ? | Shaken | |
| | | | | | |
| 1055 | 57 | 300 | ~ | Unshaken | |
| 1056 | 57 | 2,900 | ~ | Shaken | |
| | | | | | |
| | | | | After Tech Law sampling | |
| 1242 | 58 | 1,480 | 0 | Unshaken | |
| 1243 | 58 | 27,200 | 27,000 | Shaken | |

At CR652, Bathtub Faucet.

| Time | Temp | TVA-1000b | GEM-2000 | Comments | |
|------|------|--|--|-------------------------|--|
| | (°F) | CH ₄ (peak ppm _v) | CH ₄ (peak ppm _v) | | |
| | | | | After Tech Law sampling | |
| 1214 | 51 | 2,600 | 0 | Unshaken | |
| 1215 | 51 | 19,200 | 13,000 | Shaken | |

Visual Evidence of Treatment Effect of Chlorination.

At around 1030, Mr. Rupert collected water samples from two locations in the CR644 trailer: 1) at the By-Pass/Pre-LGAC sample tap, and 2) at the Kitchen Sink Faucet, in 1-gal narrow-mouth plastic jugs. Both jugs were immediately capped and set out in the sun for visual observation.

Within a few minutes, the chlorine treated but pre-LGAC water sample started to turn brownish – suggesting that the application of chlorine was indeed facilitating the oxidation of metals such as Mn and Fe, resulting in their subsequent precipitation. On the other hand, even after several hours, the post-LGAC water sample (i.e.; water that was subjected to chlorination and then de-chlorination/filtration via LGAC) remained completely clear – suggesting: 1) the precipitated contaminants were successfully removed and/or filtered, and 2) oxidation reactions resulting in the precipitation of metals had ceased. The later finding is also supported through the observation of no chlorine smell in the Post-LGAC or fully treated water. Whereas, the Pre-LGAC water sample exhibited the smell of residual chlorine.

Dosing of Chlorine (Clorox) Solution.

The CFTs for both the CR644 and CR652 treatment systems are 35-gal plastic vessels, 18 inches (in) in diameter and 32 in tall. Therefore, each vertical inch of tank volume equals 1.1 gal or 4,180 milliliters (mL).

On the morning of July 3, 2012, the chlorine dosing rates for both the CR644 and CR652 treatment systems were noted as follows. A piece of duct tape was placed on the outside of each CFT to mark the initial volume of chlorine solution. Time of the placement of the tape was noted. After several hours, both tanks were visited to note the level in the tanks. The observations were as follows:

At the CR644, the level in the tank had dropped by approximately 0.75 inch over a period of 183 minutes (start time 0921 and end time 1224). This amounts to a chlorine dosing rate of 12 mL per gal of water processed through the CR644 system [(4,180 mL per inch x 0.75 inch) / 183 min / 1.43 gpm].

At the CR652, the level in the tank had dropped by approximately 0.5 inch over a period of 252 minutes (start time 0930 and end time 1330). This amounts to a chlorine dosing rate of 4.14 mL per gal of water processed through the CR652 system [(4,180 mL per inch x 0.5 inch) / 252 min / 2 gpm].

Water Sampling by TechLaw for Manganese.

On July 3, 2012, after several hours of operation of the CR644 and CR652 POE treatment systems on the HW08 well water, personnel from TechLaw, Inc. (Suddha Graves and Brian Burris) collected several water samples, pre- and post-POE treatment systems. The water samples were analyzed for Mn. Based on the Final Analytical Report (USEPA 1207005FINAL DAS R34015 07 11 12 1828) dated July 11, 2012, issued by EPA Region 3 Environmental Science Center, Fort Meade, Maryland, the results of the manganese concentrations in the untreated and treated water at the Ex.6-Personal Privatery | residences are as follows:

| Manganese (Mn) concentration (μg/L) in water at the [Ex. 6-Personal Privacy] Residences on July 3, 2012 | | | | | | |
|---|-------------------------|----------|--------------------------|----------|--------------------------|----------|
| | Before Treatment at the | | Treated water at Kitchen | | Treated water at Bathtub | |
| | Well Head HW08 | | Faucet at CR644 | | Faucet at CR652 | |
| | Unfiltered | Filtered | Unfiltered | Filtered | Unfiltered | Filtered |
| Sample | 1,170 | 1,150 | 176 | 132 | 1,070 | 1,030 |
| Duplicate | 1,150 | 1,160 | | | | |
| Average | 1,160 | 1,155 | 176 | 132 | 1,070 | 1,030 |

Note: The USEPA established Secondary Maximum Contaminant Level (SMCL) or the Secondary Drinking Water Standard for Manganese is 50 µg/L.

FINDINGS

Based on the observations made during the POE system maintenance and startup activities, the following can be stated about the worthiness and/or limitation of the existing POE water treatment systems at the two [Ex. 6 - Personal Privacy | residences; CR644 and CR652:

Related to Mn Treatment and System Performance

O The performance of the existing POE system with respect to Mn removal appears to depend significantly on the proper dosing of the chlorine solution. At CR644, where the chlorine solution feed rate was 12 mL per gal of water processed, Mn was removed on the order of 85% (from about 1,160 to 176 μg/L). In contrast, at CR652, where the chlorine solution feed rate was 4.14 mL per gal of water processed (about 1/3rd of that at CR644), there was very little removal of Mn.

Removal of Mn from the well water appears to be feasible with the existing POE systems - which are based on the chlorination/de-chlorination methodology. However, the method is not quite reliable and/or forgiving. As per [5x.4.css] the POE system provider, the operation of the CFP is simply on an "Off or On" basis, which is governed by the flow sensor switch on the feed water line. The CFP is setup to come "ON" at a feed water flowrate of 0.5 gpm, and it will continue to inject chlorine solution into the feed stream at a fixed (preset) rate even if the water flowrate increased significantly. On the other hand, if the rate of water consumption in the home at a given time was less than 0.5 gpm, there would not be any chlorine dosing, and thus no treatment of dissolved Mn, Fe or other similar constituents.

In addition, the optimal performance of the system also depends significantly on the physical involvement of the home owner on a daily basis; for the purging of the sediment from the CCT and ensuring there is sufficient chlorine solution in the CFT. These aspects of the existing POE system make it more susceptible to sub-optimal performance and/or prone to maintenance issues.

Related to Impact of Methane on Water Quality and System Safety

- The water from well HW08 outside the Ex.5-Personal Privacy | residences contains measurable levels of methane gas. Screening of the vapor phase in contact with the well water with field gas monitors (TVA-1000b or GEM-2000) suggests vapor phase CH₄ concentrations ranging from hundreds of ppm_v to percent levels (i.e., greater than 10,000 ppm_v). The highest CH₄ concentration of 8.8% (or 88,000 ppm_v) in the vapor phase was recorded from the headspace of a vigorously shaken HW08 water sample bottle. This concentration is well within the flammability range of 5 to 15% CH₄ in air (http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html). The highest vapor phase CH₄ concentration in an unshaken HW08 water sample was recorded at 4% (or 40,000 ppm_v), which is just shy of the lower explosive limit (LEL) for CH₄, which is 5%.
- Typically, at normal atmospheric conditions [at pressure = 1 atmosphere (atm), and temperature of 68°F] the solubility of CH₄ in water is approximately 23 milligrams per liter (mg/L). At a typical groundwater temperature of 50°F, the solubility is approximately 28 mg/L (http://www.engineeringtoolbox.com/gases-solubility-water-d 1148.html). This means that, at 50°F, if a mass of water was in contact with a mass of pure CH₄ (gas) at 1 atm pressure, and if the two phases were allowed to attain equilibrium, the water (solvent) phase would hold up to 28 mg/L of CH₄. In such a case, the mole (or volumetric) fraction of CH₄ in the vapor phase would be 1.0 (or 100%). As per Henry's Law (http://en.wikipedia.org/wiki/Henry%27s law), if the mole fraction of CH₄ in the vapor phase was to drop to 0.5 (or 50%), the new equilibrium concentration of CH₄ in the water phase that can be sustained would be 14 mg/L (0.5 x 28 mg/L). Conversely, if the water phase had 14 mg/L of CH₄, the equilibrium concentration (volumetric) in the vapor phase would be 50%. The other 50% would have to be some other gas (or a mixture, such as air). Applying the Henry's Law (rule), it means that under ideal (equilibrium) conditions, when CH₄ concentration in water reaches 1.4 mg/L (0.05 x 28 mg/L), the vapor phase CH₄ concentration can be expected to reach 5%, or the LEL, which is the lower limit for flammability range (5 to 15%) for CH₄. Interestingly, the upper flammability limit for CH₄ being 15% means that if CH₄ in water was 4.2 mg/L or greater, the vapor phase concentration would be 15% or more, putting it outside the flammability range. In other words, the vapor phase pocket would be too rich in CH₄ to support a flame. But having said that, from a practical stand point, even if the center of the CH₄ rich pocket could not support a flame, if the pocket was to dissipate and get diluted, it would then become suitable for sustaining a flame, or an explosion. Thus, from a safety perspective, a water phase CH₄ concentration of more than 1.4 mg/L could lead to a potentially hazardous situation.

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Trace amounts of CH₄ in drinking water may not, in itself, be toxic or hazardous. Also, when CH₄ and chlorine (Cl₂) are mixed together in the absence of light at room temperature nothing happens. However, at higher temperatures or under ultraviolet (UV) irradiation, the two will react to form chloromethane (CH₃Cl) (http://chemwiki.ucdavis.edu/Organic Chemistry/Hydrocarbons/Alkanes/Chlorination of Metha ne and the Radical Chain Mechanism). Depending on reaction conditions, and when sufficient Cl₂ is available, chlorination of CH₄ may yield other chloromethanes (CMs); dichloromethane, chloroform and carbon tetrachloride (http://en.wikipedia.org/wiki/Free radical halogenation). Activated carbon, for all practical purpose, is not capable of removing CH₄ from water. Thus, CH₄ present in the feed water coming from well HW08 will travel through the existing POE treatment train unimpeded. In all likelihood, any CM generated upstream of the LGAC, should be sequestered by the LGAC. Though the probability of CM generation in the existing POE systems is small, there remains a potential for CM generation, should the LGAC's Cl₂ adsorption capacity be exhausted, and the excess Cl₂ and CH₄ containing water goes through the water heater, for example, or if the treated water was subjected to light or UV radiation. Strict monitoring of the life and performance of the LGAC in the existing treatment system is therefore critical for safeguarding against the inadvertent exposure of the residents to CMs. Furthermore, at CR644, if otherwise treated water, but containing CH₄, was used for the [Ex.6-Personal Privacy], the potential of CM generation increases due to the routine chlorination of the pool water and exposure to the sun. Use of the HW08 water for the Ex. 6-Personal Privacy as long as it is known to contain CH₄, is not recommended.

REFERENCES

- 1. USEPA 1207005FINAL DAS R34015 07 11 12 1828. Final Analytical Report on Groundwater Sampling at Dimock Residential Groundwater Site, Dimock, PA. July 03, 2012.
- Gases Explosive and Flammability Concentration Limits.
 (http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html)
- 3. Solubility of Gases in Water.
 (http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html)
- 4. Henry's Law. (http://en.wikipedia.org/wiki/Henry%27s_law)
- 5. Chlorination of Methane and the Radical Chain Mechanism.

 (http://chemwiki.ucdavis.edu/Organic_Chemistry/Hydrocarbons/Alkanes/Chlorination_of_Methane_and_the_Radical_Chain_Mechanism)
- 6. Free-radical Halogenation. (http://en.wikipedia.org/wiki/Free radical halogenation)